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J. H. Sturdivant and **Linus Pauling** (Pasadena): **Note on the Paper of A. Schröder: Beiträge zur Kenntnis des Feinbaues des Brookits usw.** (With 2 figures.)

We have recently found[4]) the space-group symmetry of brookite, the orthorhombic form of titanium dioxide, to be that of V_h^{15}. In our space-group determination, use was made of the presence or absence of reflections on Laue photographs only. Reflections from all types of bipyramidal planes were observed, requiring that the structure be based on the simple orthorhombic lattice Γ_0. No first-order reflections were observed from prism planes of the following classes, although many such planes were in positions favorable to reflection:

$$k = 0 \text{ and } l \text{ odd};$$
$$l = 0 \text{ and } h \text{ odd};$$
$$h = 0 \text{ and } k \text{ odd}.$$

The space-group criteria for V_h^{15} are that no odd-order reflections shall occur from just these planes. These criteria were afterwards found to be satisfied by reflections observed on several rotation photographs.

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1) Gemeint ist dabei die Deformation der farblosen gelösten Ionen Hg^{++} und J^- bei ihrer Vereinigung zum Salz.
2) H. Ley, Z. angew. Ch. **41**, 845. 1928.
3) G. Scheibe, Chem. Zentralbl. 1927, II. 2151. Z. Elektrochem. **34**, 497. 1928.
4) Linus Pauling and J. H. Sturdivant, Z. Krist. **68**, 239. 1928.

On page 241 of our paper we pointed out the desirability of basing a space-group determination on Laue photographs rather than on rotation photographs, on account of the small chance of error in assigning indices to the planes producing Laue spots and the much larger uncertainty in identifying planes producing reflections on rotation photographs. An example of an incorrect choice of space-group arising from the use of rotation photographs was cited.

A. Schröder[1]) has published data on rotation photographs of brookite which are incompatible with the space-group V_h^{15}. He reports the observation of odd-order reflections from the following classes of prism planes:

$$k = 0 \text{ and } l \text{ even},$$
$$l = 0 \text{ and } h \text{ even},$$
$$h = 0 \text{ without restriction.}$$

Reflections reported by Schröder which do not satisfy the criteria for V_h^{15} are: (051), (032), (052), (013), (033), (012), (015), (031), (034).

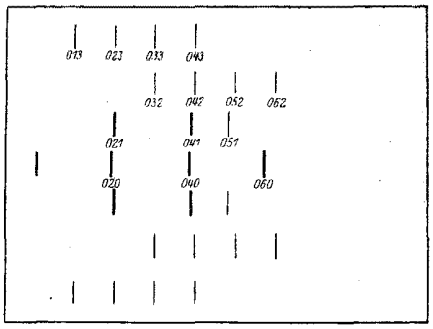

Fig. 1.

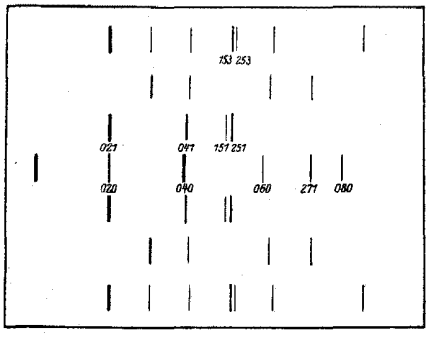

Fig. 2.

Fig. 1. Diagram of Schröder's rotation photograph No. 3, showing his assignment of indices. The X-ray beam was incident on (010), the crystal rotating through 20° about [001].

Fig. 2. Diagram of a photograph made by the writers with the crystal oriented as for Fig. 1, but rotating through 45°. The proper assignment of indices is shown for those lines which it is considered practical to identify.

On our Laue photographs the following planes, listed in Table III of our paper, failed to reflect in the first order, although in position to do so: (051), (05$\bar{1}$), (032), (015), (031), (034). The following planes not listed in our paper also failed to produce Laue spots, although in a position to reflect radiation of the wave-lengths indicated: (052) at $n\lambda = 0{,}28$ and 0,38 Å, (013) at $n\lambda = 0{,}59$ Å, (012) at $n\lambda = 0{,}64$ Å. These observations show that eight of the nine reflections reported by Schröder to disagree with the criteria of V_h^{15} do not occur on Laue photographs. The presence or absence of the remaining reflection, (033), cannot be determined from Laue photographs on account of its superposition on (022).

There is additional evidence that Schröder's supposed observation of reflections which we find not to occur arose from error in his assignment

1) A. Schröder, Z. Krist. **67**, 485. 1928.

of indices to reflections on rotation photographs. The distance between reflections due to planes of form $(0kl)$ and of form $(1kl)$ on a photograph made with the film 10 cm. from the crystal is 0,7 mm. Measurements of the position of the central point of a given line referred to the central point of the undeviated image can accordingly scarcely be rendered sufficiently trustworthy to decide between two possible sets of indices differing so slightly as $(1kl)$ and $(0kl)$. The distance between two reflections which lie close together, however, can afford a more decisive test. We have made a rotation photograph with the X-ray beam incident on the (010) plane of brookite, and with the crystal rotating through 45° about the c-axis; the crystal-to-film distance was 10 cm. and the $MoK\alpha$ radiation was isolated with a zirconia filter. This photograph corresponds to Schröder's photograph No. 3, reproduced with his assignment of indices in fig. 1. On our photograph, the principal reflections of which are represented in fig. 2, there appears on the right of the line numbered (051) by Schröder a slightly stronger reflection. These two reflections are due to two of the planes (051), (151), and (251). In both lines, the $K\alpha$ doublet was resolved. We calculate the following theoretical separations for the $MoK\alpha_1$ reflections from these planes:

(051) to (151) = 0,074 cm.
(051) to (251) = 0,221 cm.
(151) to (251) = 0,147 cm.

The separation of the two $K\alpha_1$ reflections was measured on the film as 0,143 ± 0,003 cm. These two reflections are accordingly due to the planes (151) and (251), and Schröder's assignment of one of them to the prism plane (051) is incorrect[1]).

The same error was no doubt made in his assignment of indices to the other reflections.

Summary.

It is shown that Schröder's reported observation of X-ray reflections from brookite not allowed for a structure based on the space-group V_h^{15} is due to error in his assignment of indices to lines on rotation photographs.

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1) The occurrence on Schröder's photograph of the reflection from (151) and not that from (251) arises from his small angle of oscillation of the crystal (20°).